Next Generation Membrane Materials and Structures for Energy-Efficient Gas Separations

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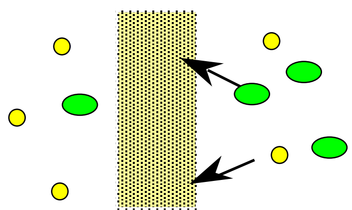
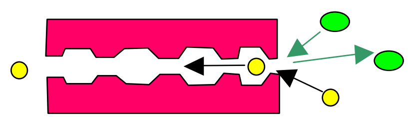
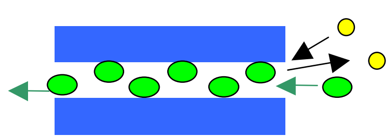
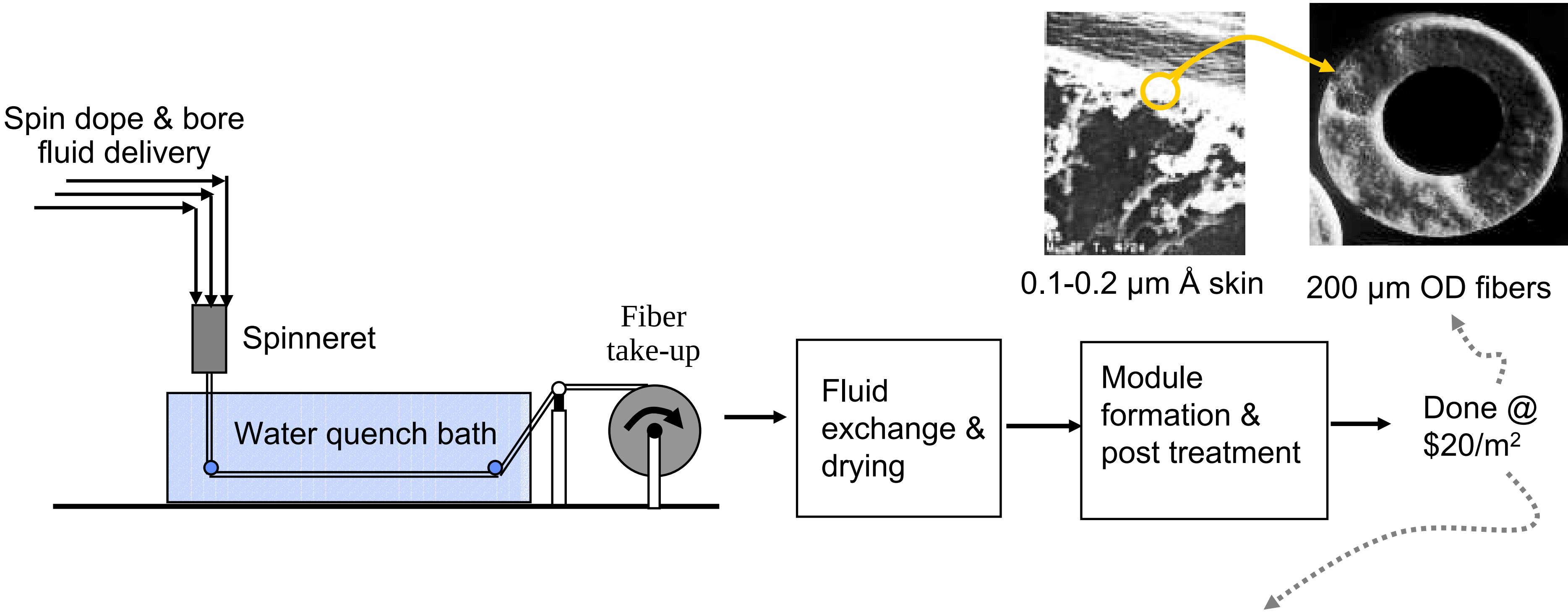
- Revolutionary ***vs.*** evolutionary advancement strategies
- Hybrid materials– the key evolutionary step
- Fundamental hurdles to making this evolutionary step
- Conclusions & projections

Sorption-diffusion membranes dominate large scale applications

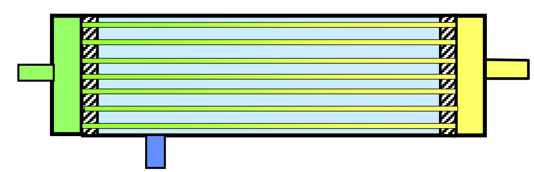
Sorption-Diffusion Permselectivity, $\alpha_{AB} = \dfrac{[P_A]}{[P_B]} = \dfrac{[S_A]}{[S_B]} \dfrac{[D_A]}{[D_B]}$

Type	Key Sorption-Diffusion Membrane Types
A. Polymeric solution-diffusion	 Flexible polymers enable selective permeation of the smallest **and/or** the most condensable (soluble) penetrant --- but encounter limits in α_{AB} vs P_A
B. Molecular sieving (**small pore** zeolites, & carbons)	 Rigid morphology enables highly size selective diffusion jumps favoring **smallest size** penetrant --- but large modules are expensive & hard to make.
C. Surface diffusion (**large pore** zeolites, glasses, carbons)	 Rigid morphology enables **most condensable** penetrant to exclude less condensable (often smaller) penetrant ---again, large modules are expensive & hard to make.

State-of-the-art hollow fiber spinning processes (50-100 meters/min) allow multiple parallel lines for high throughput, low membrane costs

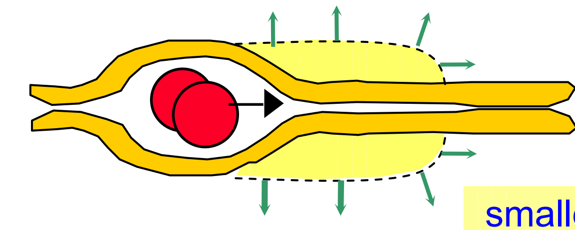


>10⁶ fibers, 200 µm OD fiber with 0.1-0.2 µm Å skin in module is currently possible

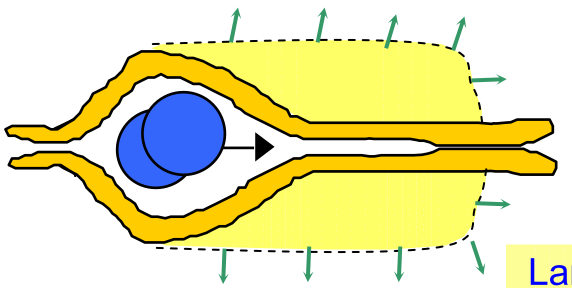


For a large membrane area applications, current membranes (without pretreatment costs) can cost 50% less than competitive technologies– but pretreatment needs sometimes greatly reduce this advantage— **more robust, but still economical** membranes are needed!

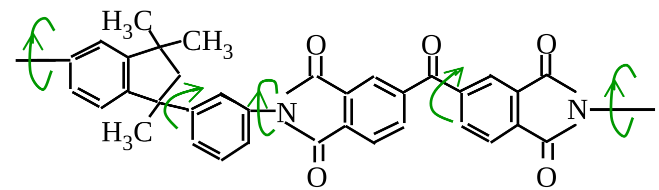
If the "zone of activation" polymers cannot be controlled with ever-increasing for accuracy–can selectivity still be increased?



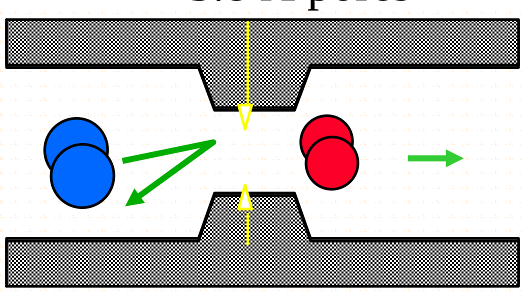
smaller zone of activation for O_2



Larger zone of activation for N_2

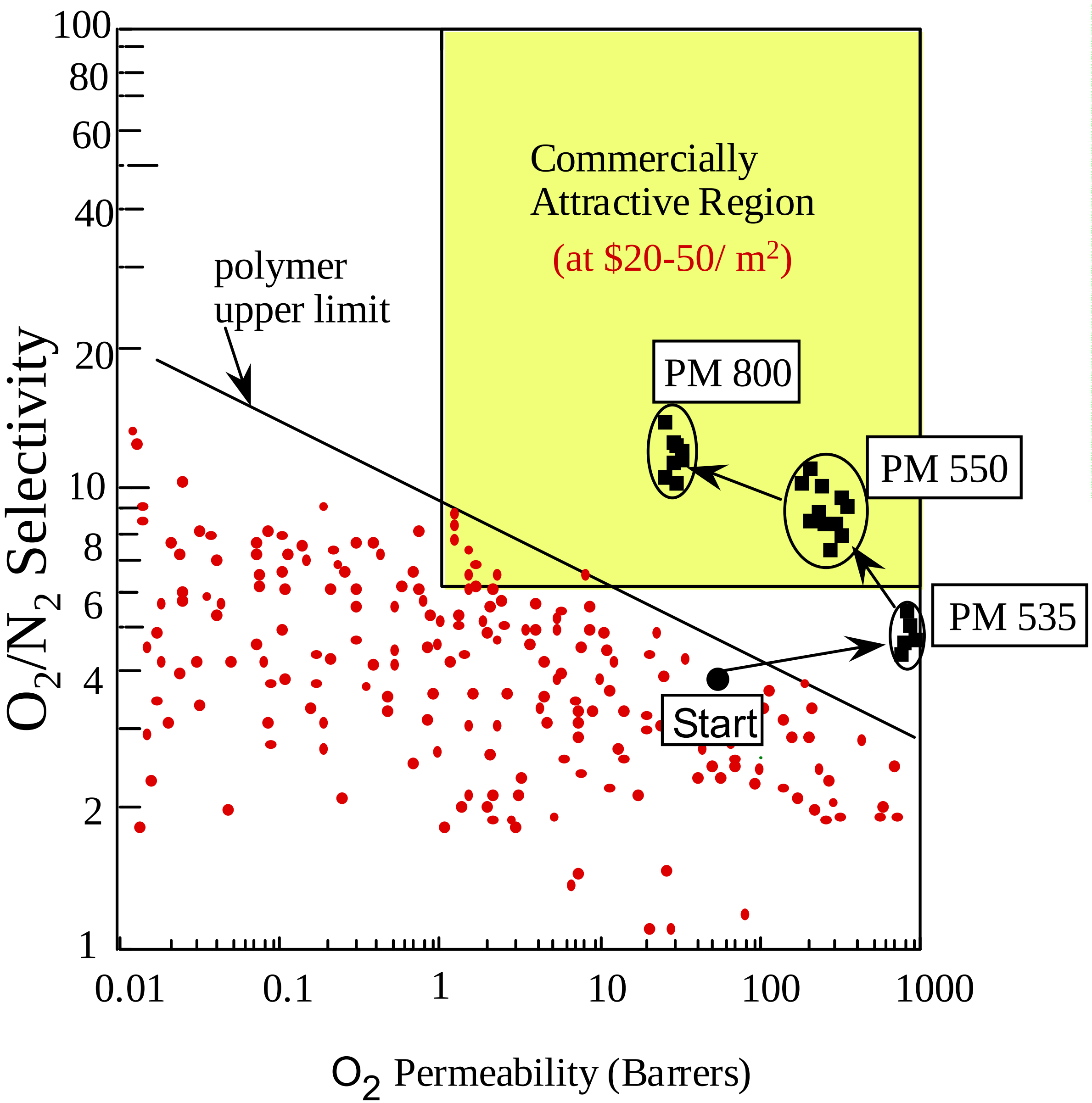


~ 3.8 Å pores



Since thermal & chem. stability & selectivity ↑ for mol. sieve carbons and/or inorganics, do they offer actual solutions for large scale applications?

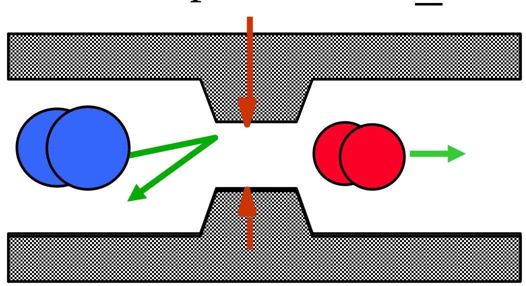
Tailored carbons & inorganic membranes offer a "technical" solution for many gas & vapor applications



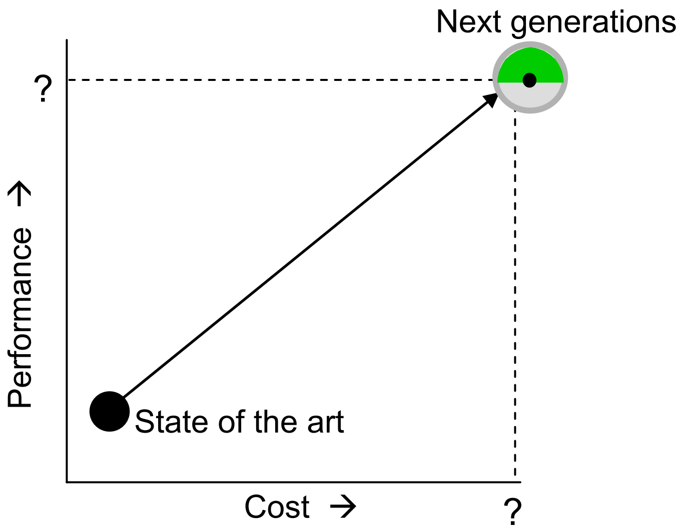
2-4 orders of magnitude faster processing for polymerics allows much lower \$/m^2 vs.carbons & inorganics.

Additional innovative research is needed to provide carbons & inorganics a place in <u>large scale</u> applications.

controllable pore sizes $\pm$ 0.1 Å



Moving to the Next Generation Involves Performance & Cost Issues



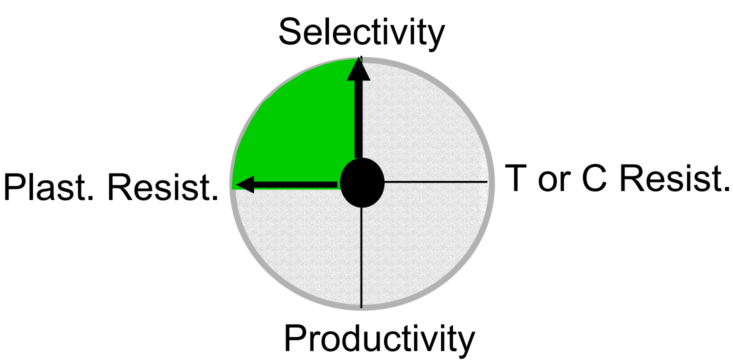
"Performance Increase" can mean different things:

I : Increased selectivity

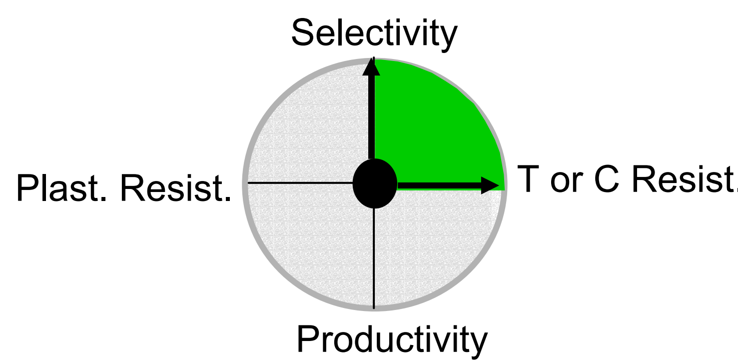
II : Increased productivity (useful but less critical need)

III : Increased plasticization resistance--maintain selectivity

IV : Increased thermal (T) or chemical (C) resistance



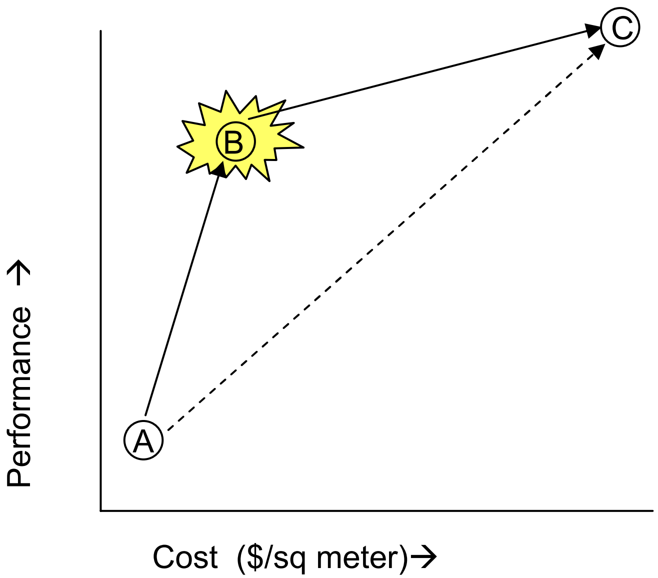
Vs.



Intrinsically more selective & more swelling resistant— more **broadly applicable**

Intrinsically more selective & more thermally or chemically resistant—useful, **specialty** applications

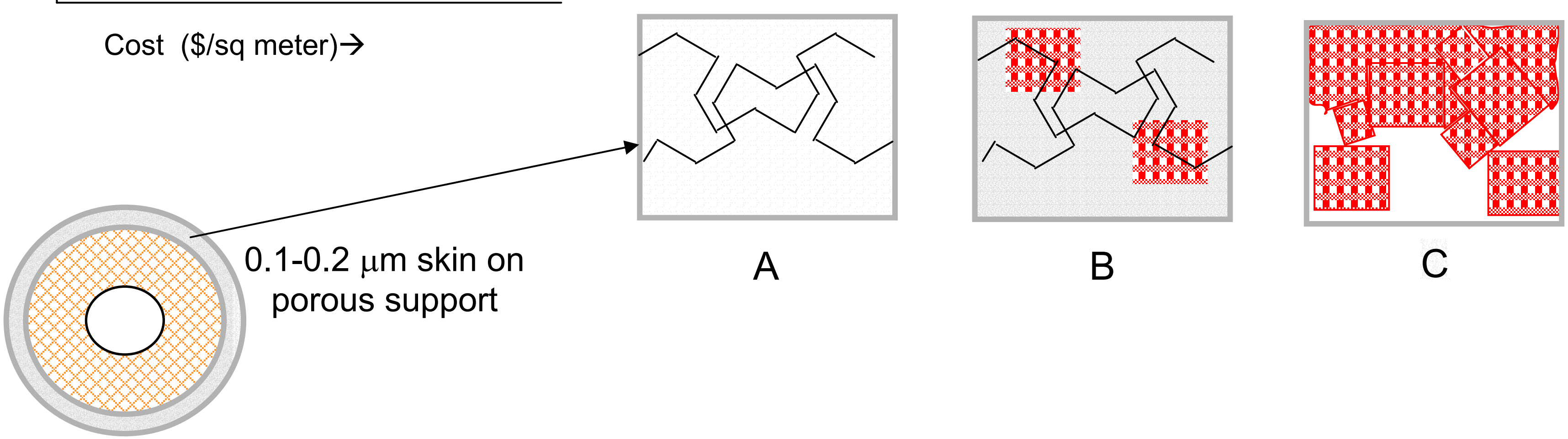
Revolutionary (A→C) vs. Evolutionary (A→B→C) Strategies



A: current organic polymers

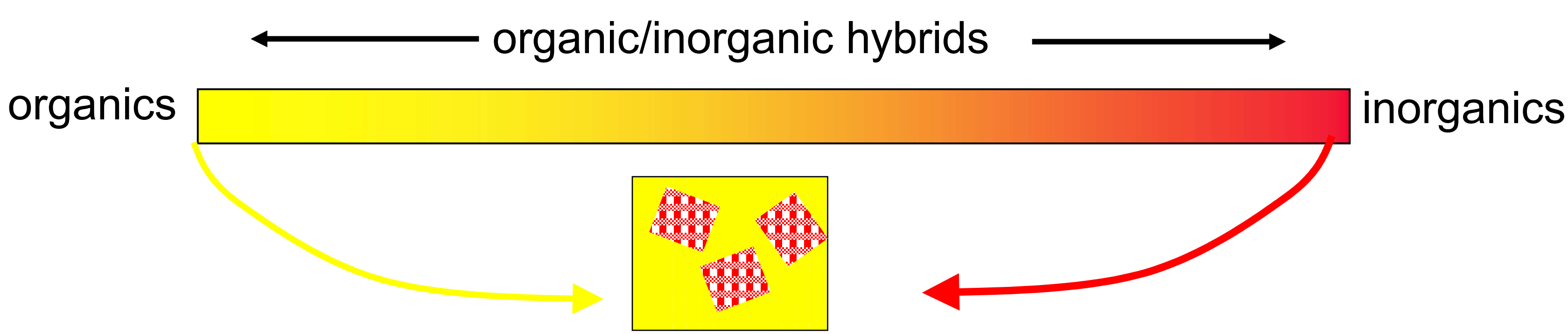
B mixed matrix hybrids

C: pure inorganics or carbons



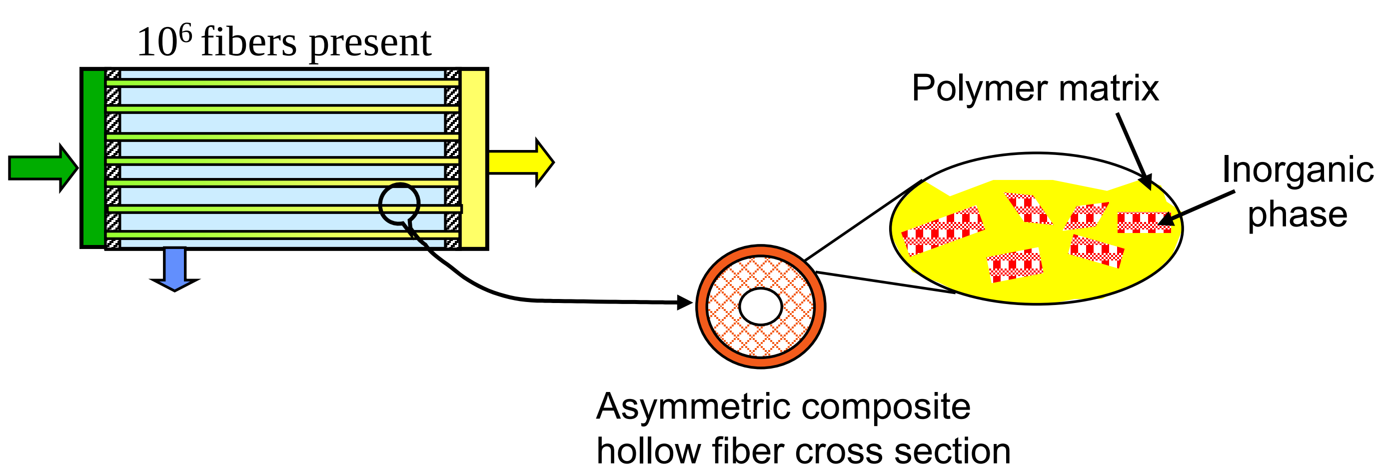
Asymmetric hollow fiber cross section—current state of the art

Organic-Inorganic Hybrids May Maintain Low Costs of Current Organic Polymers & Approach Performance of Inorganics



Integrate into current membrane manufacturing process (100 m/min)

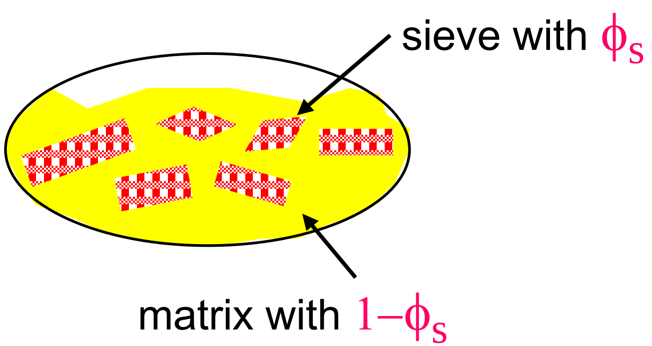
Solution Make-up → Spinning into non solvent quench bath → Fluid exchange & drying → Module formation → Done @ $50/m² vs. $20/m² now!



How to Achieve Practical Mixed Matrix Membranes? - - the first step involves sieve & polymer material "matching"

A fundamental framework exists to guide "materials selection" ----

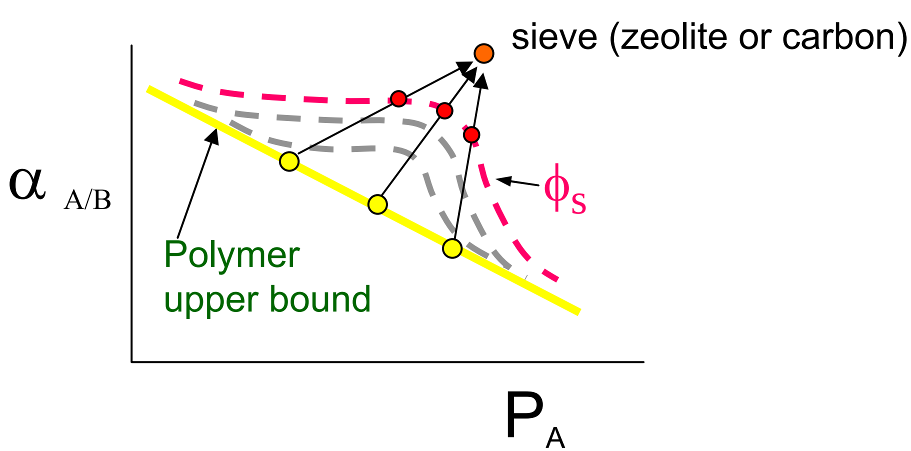
For a selected sieve & volume fraction (ϕ_s), composite models predict "Enhancement Regions" above polymer upper bound line. (Sieve permeability can be "calibrated" using a reference polymer & then matched to appropriate upper bound polymer matrix)



e.g. Maxwell model for component **A** or **B**

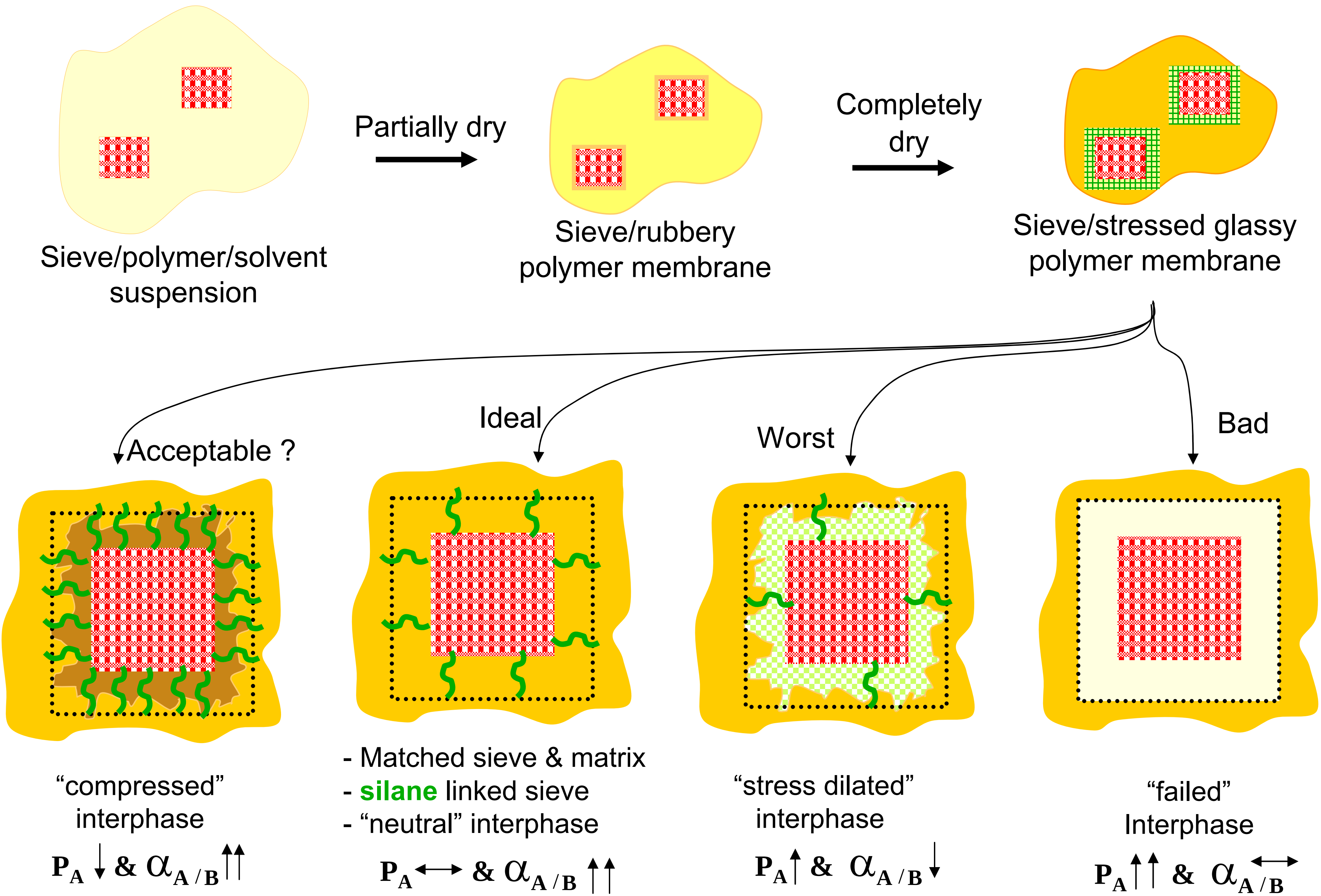
$$\mathbf{P}_c = \mathbf{P}_m \left[\frac{\mathbf{P}_s + 2\mathbf{P}_m - 2\Phi_s(\mathbf{P}_m - \mathbf{P}_s)}{\mathbf{P}_s + 2\mathbf{P}_m + \Phi_s(\mathbf{P}_m - \mathbf{P}_s)} \right]$$

$\alpha_{A/B} = \mathbf{P}_{cA}/\mathbf{P}_{cB}$ from above model



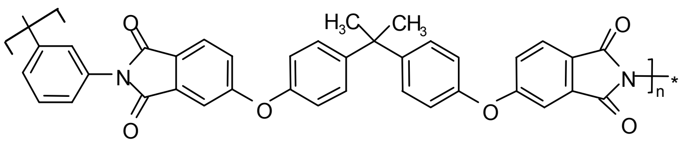
. . . But the world includes nonideal realities that must be controlled !

Non-Ideal Effects: Shrinkage/Coupling/Compatibility Issues

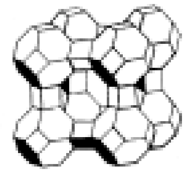


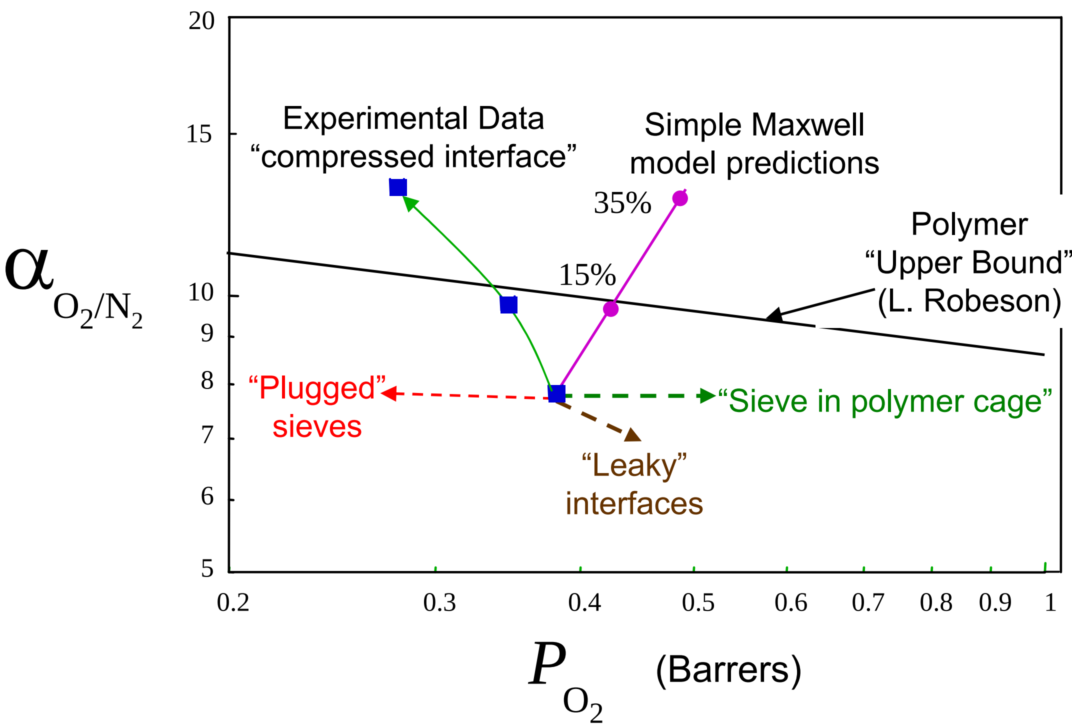
Ultem®-4A Zeolite Mixed Matrix Materials

Ultem® 1000 polyetherimide (GE)
Tg ~ 220° C

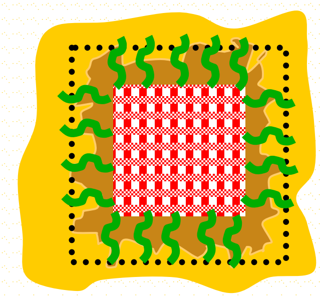


Zeolite 4A
Molecular Sieve

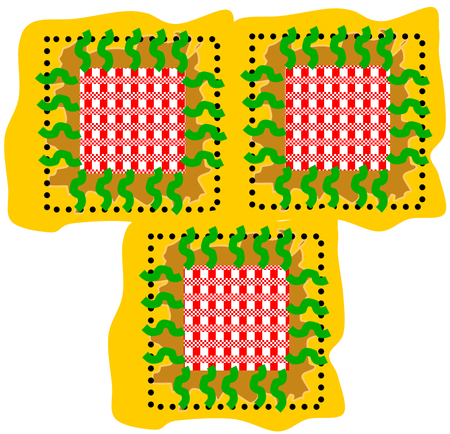




Performance above upper bound α_{O_2/N_2} > **13** for pure & <u>mixed gas feeds</u> show expected selectivity but lower permeability--- suggesting a “compressed interface”



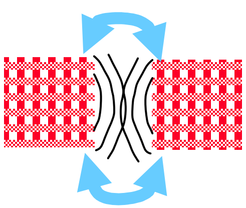
Key fundamental questions impact materials & spinning topics

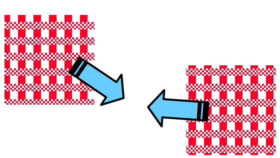


- How are sub-nanometer level properties of flexible chain organic polymers affected near surfaces of rigid submicron solids?
  - transport properties in the *nanometer* domain near solid surfaces *versus* the bulk polymer “far” from the surface?
  - effective mechanical properties (modulus & transport properties) as “zones of influence of dispersed solids overlap in casting dopes & vitrified hybrid material ?

- How do millisecond time-scale events during formation of asymmetric skinned structures affect properties noted above compared to the case of a “simple” solution cast dense film?

Van der Waals attractions





Collision-induced aggregations

Conclusions, projections… and next steps needed:

- Hybrid materials can expand membrane-based gas separation applications

- Morphologies at multiple structural levels and the impact of processing approaches on these morphologies must be understood better

- Control of nanoscale interfaces between the domains in hybrid materials is the *key hurdle* to inhibiting the transition from lab-scale to a production scale

- Better ways to probe adhesion and the resulting influence on the transport properties of the interphase region between the two phases is needed

- Key questions involved in this technology push the state of the art of theory
- & characterization techniques in the materials science & engineering fields

- Involvement of diverse “non-membrane” materials science & engineering
- experts is badly needed in this field